



Letter to the Editor

Comments on Kalamaras et al., *Appl. Catal. B: Environ.* 136–137 (2013) 225–238, discussing the difficulty in assessing reactant and product readsorption effects in SSITKA-type work

Dear Editor,

A study of the water–gas shift (WGS) reaction (Eq. (1)) was recently published in this journal by Kalamaras et al. that reported steady-state isotopic transient kinetic analysis (SSITKA) and diffuse reflectance FT-IR spectroscopic (DRIFTS) data recorded over Pt–Ce–La-based catalysts [1].



Such combination of advanced characterization techniques is rare and the authors should be acknowledged for carrying out such sets of time-consuming and difficult experiments. While I agree with most of the findings reported by the authors, there are yet a few points on the interpretation of the results that I would like to raise to the attention of the authors and, following preliminary constructive communications between Prof. Efstathiou and myself, I hope that my comments and the authors' reply will clarify further these concerns and/or misunderstandings for a larger audience.

1. CO₂ adsorption and stability

CO₂ is the major gaseous reaction product alongside H₂ and because of its acidic character there is a significant concentration of adsorbed CO₂ (noted here “CO₂(ads)”) over basic centers present at the surface of ceria and lanthana in the form of, e.g., carbonates, carboxylates and hydrogenocarbonates. A large fraction, if not all, of these CO₂(ads) are reversibly adsorbed under reaction conditions as shown in a previous study carried out on similar catalysts (see in particular Sections 3.2 and 3.4 and Fig. 9 in Ref. [2]). Reference to this earlier work of ours is essential because it showed that a fraction of CO₂(ads) were strongly bound and stable under an Ar or H₂ atmosphere, but then readily exchanged when exposed to isotopically labeled CO₂.

Such changing reactivity of samples comprising ceria is partly explained by a difference of surface oxidation state of Ce due to the presence of partially reduced Ce^{III} centers. CO₂(ads) are more strongly bound to Ce^{III} sites than to Ce^{IV}. In fact, the formation of carbonates strongly bound to Ce^{III} was proposed as the main cause of deactivation of Au/CeO₂ and Pt/CeO₂ catalysts, which could be overcome by adding some O₂ to the WGS feed [3]. It is therefore clear that any change of the oxygen chemical potential of the feed (whether it is induced by changing the concentration of CO₂ [2], H₂O or O₂ [3]) will potentially lead to marked differences in the stability of CO₂(ads).



In the paper by Kalamaras et al. [1], the authors referred to earlier papers of their group to estimate CO₂ readsorption; for example data relating to the adsorption and desorption of CO₂ in inert gases [4]. This type of experiments is insufficient to correctly estimate reversible and irreversible CO₂ adsorption, for the reasons discussed above, as the level of CO₂(ads) isotopic exchange under reaction condition (i.e. in the presence of CO, H₂ and H₂O) is likely to be different from that observed under inert gases.

2. The complexity of measuring CO₂ intraparticle readsorption

Kalamaras et al. [1] have correctly addressed the effect of interparticle CO₂ readsorption by varying the catalyst mass present, and were able to correct for this effect (similarly to earlier data reported in Fig. 9 of Ref. [4]). However, *intraparticle* readsorption in the catalyst pores of the CO₂ produced was not addressed. The occurrence of intraparticle readsorption is very difficult to estimate and eliminate, as indicated by Shannon and Goodwin [5]. One could envisage feeding some CO₂ along the CO/H₂O feed to limit CO₂-product readsorption, but this may not even lead to a clear answer. The extent of CO₂ readsorption (both intra and interparticle) is likely to be negligible only on poorly basic catalysts, such as zirconia. As a matter of fact, neither carbonate nor carboxylate species were observed at the surface of a Pt/ZrO₂ under reaction conditions and the size of the C-pool was found to be well below that corresponding to the number of Pt surface atoms [6].

In conclusion of points (1) and (2), I believe that the size of the C-pool (concentration of carbon-containing precursors of the reaction product CO₂) was likely to be significantly overestimated in Ref. [1], as it also accounted for species that were merely due to inevitable CO₂ readsorption in the pores of the catalyst particle in which CO₂ was formed.

3. Size of the H-pool

To me, the large H-pool observed in Ref. [1] (up to 16 times the amount needed to cover all surface Pt atoms) could be largely due to the scrambling of H₂O and D₂O with surface –OD or –OH during “WGS-irrelevant” water adsorption/desorption processes, leading to a large over-estimation of the H-pool of true reaction intermediates. Note that the expected difference of surface reactivity under transient and steady-state conditions (see Section 1 above) makes difficult the combination of SSITKA data and non-isotopic transient data (involving a change of the chemical potential of one or more elements). To me, the level of HD production during D₂O and H₂O transients in Ar, which is cited from earlier papers by the authors, does not bring any relevant information neither on the reduction of water to H₂ in the presence of CO nor on the extent of water readsorption prior to reaction.

4. C-/H-pool and main reaction pathway

A general comment arises from the collection of SSITKA-DRIFTS data in which the WGS activity is tentatively correlated to the observed reactivity of surface species as in the paper in question [1]. The data reported in Sections 3.4 and 3.5 of Ref. [1] clearly revealed a certain level of reactivity of species such as the formates seen by DRIFTS. However, it must be clearly stressed that there could be other important surface intermediates not directly observable by DRIFTS, e.g., another type of formates of a concentration too small to be detected in the signal of “slowly reacting” formates or carboxylates CO—OH, as proposed by many theoreticians. Redox-type routes, which may not lead to any IR-observable intermediates, could also be important, as proposed by Kalamaras et al. [1]. Therefore, it would be useful to estimate the contribution of DRIFTS-observable formates based on the product of the first-order rate constant of exchange of formates (determined by SSITKA-DRIFTS data) and a calibration curve as described elsewhere [7–9]. This calculus leads to the upper limit of the rate of CO₂ formation associated with these formates, which assumes that each formates decomposed to CO₂ + H₂ (and not to CO + H₂O). In these references dealing with highly active WGS catalysts [7–9], the highest possible contribution of DRIFTS-observable formates was shown to be lower than ca. 15% of the overall WGS activity.

These earlier findings, in agreement with those reported by Kalamaras et al. [1], underlines that there are at least two reaction pathways that are simultaneously active for the WGS over this type of materials. The C- and H-pools measured are likely to be mostly those relating to the slowest reaction pathway (minority route), comprising intermediates with the longest lifetime and highest surface coverage. In contrast, the majority route most likely involves intermediates with the shortest lifetime (i.e. high TOF) and a corresponding lowest steady-state surface coverage. Mavrikakis et al. gave a useful theoretical example on a Cu(111) metal surface [10], over which the surface coverage of the main reaction intermediate (a carboxyl CO—OH species) was calculated to be three orders of magnitude lower than that of spectator-like formates. Hence, there is always a significant risk that the pools measured by SSITKA (even in the absence of any readsorption effects) represent the concentration of the reaction intermediates that are part of the least meaningful pathway.

5. Concluding remarks

In the light of these comments, it could be useful to reassess some of the conclusions of the study in question [1], namely the

pool size of the “active” reaction intermediates, the nature of these intermediates and the nature of WGS mechanism(s) on these samples. To be fair, I did a similar misinterpretation of SSITKA-DRIFTS data in a paper of ours on the reverse WGS [11], in which the possibility of readsorption of the CO₂ reactant was overlooked and led me to propose that carbonates were main reaction intermediates, while no sufficient experimental evidence supported this specific (still unproven) conclusion. I now wish a reviewer had pointed out this shortcoming to me. In a subsequent work on WGS over Au/Ce-La oxide catalysts, we actually stressed that the readsorption of the CO₂ product made impossible the determination of the concentration of true reaction intermediates (i.e. C-pool) by SSITKA (see Section 4.3 of Ref. [7]). I hope that this discussion will be of interest to all the researchers interested in the use of SSITKA-type techniques and that the authors of Ref. [1] will be able to clarify the concerns expressed above.

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